Ta SMD capacitors with MnO_2 and Polymer Counter Electrode for Space Applications

2nd Space Passive Component Days (SPCD), International Symposium

12-14 October 2016
ESA/ESTEC, Noordwijk, The Netherlands

Ana Tomás[(1)], Cristina Mota-Caetano[(1)], Rui Monteiro[(1)], Jorge Vacas[(1)], Dr. Denis Lacombe[(2)]

[(1)]KEMET Electronics Portugal, S.A.
Road Werner von Siemens 1, Évora, 7005-639, Portugal
Email:anatomas@kemet.com
Email:cristinacaetano@kemet.com

[(2)]ESA/ ESTEC European Space Agency
Keplerlaan 1NL 2200AG, Noordwick ZH, The Netherlands
Email: denis.lacombe@esa.int

ABSTRACT

Solid electrolytic tantalum capacitors utilizing intrinsically conductive polymers as the solid cathode electrolyte have been commercially available since the mid 1990's. Components utilizing this cathode system offer numerous advantages over traditional manganese dioxide based solid electrolytic capacitors, including lower ESR, improved surge current resistance, benign failure mode and lower voltage derating requirements. In 2012 high reliability capacitors employing intrinsically conductive polymer cathodes for military and aerospace markets were successfully developed and marketed. This paper presents reliability data for low voltage, low ESR tantalum capacitors which use an intrinsically conductive polymer as the cathode. This product was developed in partnership with the European Space Agency. A new ESCC specification, ESCC3012/005 references this new product portfolio. This product is currently undergoing further qualification testing prior to being approved for ESA's QPL. Further development work is underway on an extended range high voltage, low ESR product portfolio under an on-going partnership agreement with the European Space Agency.

Two significant advantages of manganese dioxide capacitors are the proven reliability of a design that has been available since the 1950's, and the higher temperature capability of manganese dioxide compared to the polymer electrolyte. Work is underway to leverage the improved high temperature capability of manganese dioxide based capacitors to address the urgent need for high reliability, high temperature solid electrolytic capacitors. The goal of this effort is to qualify a product portfolio with rated voltage up to 50 volts and a maximum operating temperature of 150°C. This paper discusses the Evaluation Test Program selected and agreed with the European space Agency and presents the initial results from this project.

INTRODUCTION

Surface Mount technology tantalum capacitors continue to be of preference, being widely used in general electronic industry and new circuits designs due to their unique characteristics of high volumetric efficiency, high long term reliability and stability as well as a very good process compatibility. Space application segment is no exception, considering that the related applications, whether they are for space exploration programs or communication platforms, require very high reliability in sometimes extremely adverse conditions. Resulting application with increased complexity demand the development and qualification of new technology for space grade capacitors, allowing for an unavoidable and linear increase in the flexibility in the electronic design.

Historically many capabilities were successfully introduced to the market, starting with single digit ESR for decoupling at low and high voltages for input/output in DC/DC and power management. The continuous adoption to new markets can been seen in Fig.1. The introduction of design and process improvements allow the evolution in the market from terrestrial to space applications, giving the space application designers the possibility to use the advantages of the technology: (a) stable capacitance in temperature, voltage, over time and in frequency; (b) benign failure mode and (c) high volumetric efficiency.

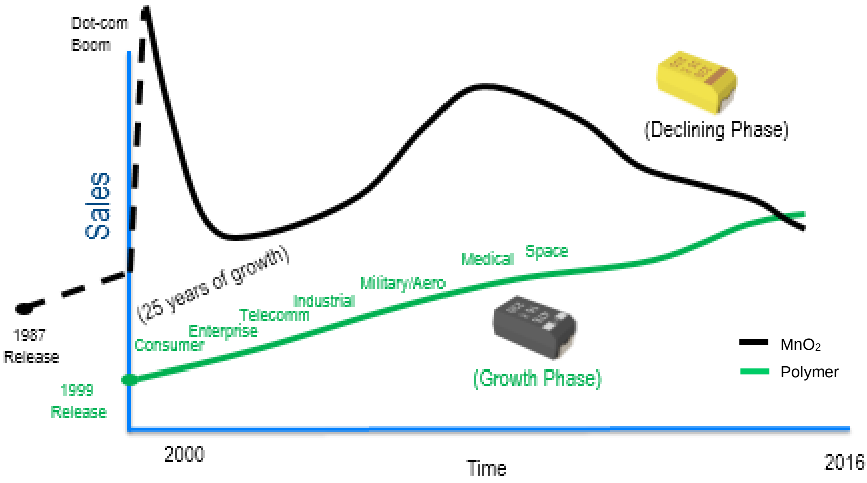


Fig.1. Historical Segment Adoption and Sales Evolution – Ta SMD Polymer MnO_2 and Polymer.

In 2012 KEMET was the 1st to market with Mil-Aero and Space surface mount tantalum polymer technology, T540 and T541 COTS Polymer Electrolytic for High Reliability Applications Series. This product offerings were first in the market with failure rate options, based on KEMET's KO-CAP Reliability Assessment Method, which utilizes accelerated conditions of voltage and temperature applied to board mounted samples to access long term device reliability. Those products are available with DLA drawings from US DoD: Dwg 04051 and Dwg04052.

Recently KEMET has focused on addressing lower ESR levels, higher voltage applications and higher operation temperatures, with a specific product line designed for European Space grade Platforms, which results and developments we intend to share in this discussion.

TA SMD CAPACITORS WITH POLYMER COUNTER ELECTRODE

Tantalum Polymer capacitors are capacitors where the counter-electrode or cathode material has been replaced by a highly conductive organic polymer in replacements of standard MnO_2 material, as we can see in Fig. 2.

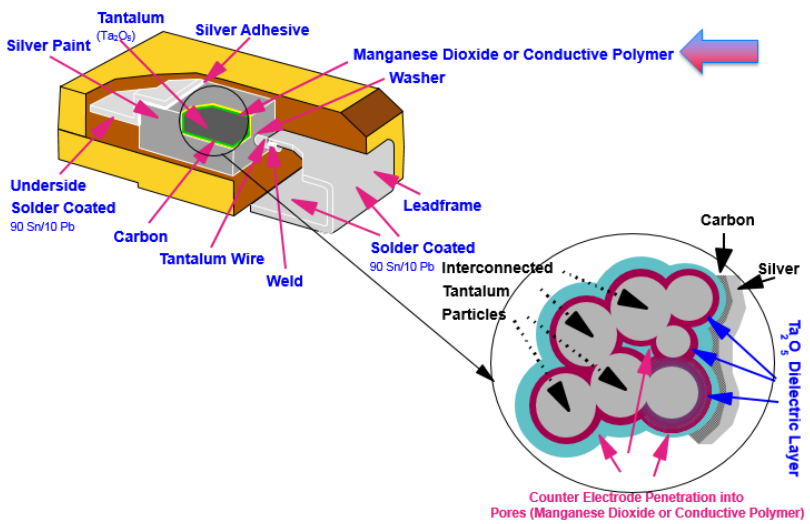
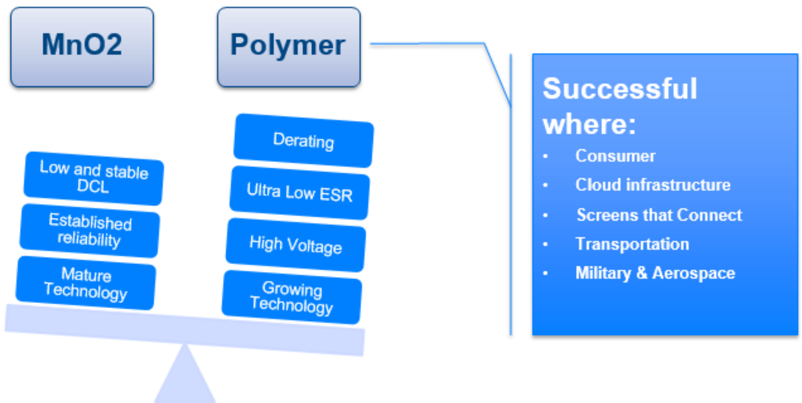


Fig.2. Tantalum Capacitor basic Construction – Polymer and MnO_2 Counter Electrode

A Capacitor is by definition an electrical circuit element used to store charge temporarily, consisting in general of two metallic plates separated and insulated from each other by a dielectric. Tantalum capacitors are electrolytic polarized capacitors, made of a central section of porous tantalum, the anode (1st plate), result of pressing and sintering of micrometric particles of Tantalum powder, covered by a Tantalum pentoxide film, the dielectric - Ta_2O_5, that grows by electrochemical anodization of the metallic anode ($2Ta+5H_2O$ - > Ta_2O_5+ $5H_2$). A tantalum wire is inserted in the center of the section and extends axially from the component connecting the negative pole. The layer of dielectric, TaO_5, is then coated with the cathode (2nd plate), a semi-conductor material that can be either MnO_2 or conductive polymer, carbon, a conductive silver layer and finally soldered and encapsulated with an epoxy compound to its known final form.

Tantalum capacitors with conductive organic polymer offer very specific design advantages over conventional MnO_2 counter electrode construction due to the higher electrical conductivity, or lower resistivity typically allow us to a 2 to 4 fold reduction in ESR. This lower ESR results in some of the most important characteristics of polymer Ta Capacitors, such as better high frequency performance, with a much later capacitance roll-off, opening a new range of high frequency circuit applications. The possibility to apply lower derating rules, the result of the soft and elastic type properties of the materials at cathode/dielectric interface and its benign non-ignition properties in a high current application makes the Polymer Tantalum capacitors a clear market trend for the years to come. Fig.3.



	Cap.	DCL	ESR	Derating	I Ripple	Failure mode	Cap. Stability
MnO2	Excellent Volumentric efficiency	Low and stable DCL	Medium/ High (0.1 up to Ohms level)	*50% * FTECH/SBDS	-	-	Over temperature and frequency
Polymer	Excellent Volumentric efficiency	Stable DCL (higher than MnO2)	Ultra Low (Down to single digit)	10% up to 10V 20% higher than 10V	Good capability	Benigne Failure mode	Over temperature and frequency

Fig.3. Comparison table for MnO_2 and polymer technology

In light of all these advantages, utilizing existing KEMET's advanced polymer technology and following the market trend and latest technology innovations, KEMET started in 2012 with ESA support, a project to develop Ta SMD polymer technology counter electrode for European Space applications up to 50V. This project was developed in two main phases: The first phase addressed the characterization and study of the failure mechanisms of the existing range of capability in the Évora plant, limited to 16V volt ratings built with first generation technology and directed to terrestrial applications, through a comprehensive and detailed Evaluation Test Plan. This allowed us to define the major needs to address the 50V voltage capability compliant with space requirements within a second phase of the project, and to qualify our existing low voltage portfolio being added to EPPL2 regulated according to specification ESCC3012/005.

Low voltage applications

To address and characterize the existing available range, up to 16V, three representative corner types were selected, based on capacitance and rated voltage, covering the spectrum of production as defined in Fig.4.

Capacitance C_n (µF)	Rated Voltage U_R		
	6.3V	10V	16V
33			60, 70
47			70
68		45, 60, 100	
100	45	55, 80	
150	45, 55		

Selected representative corner types for 6.3, 10 and 16V

Fig.4. Initial proposal for existing range samples

Considering all the possible failure mechanisms, reliability data available, and testing experience and knowledge such as Military Standards, the R&D team developed an Evaluation Test Program in accordance with ESCC nº 2263000, that allowed the determination of the failure mode mechanisms of this technology in a first phase and proof high voltage capability in a second phase. Step-stress Tests in voltage and temperature to address reliability in maximum operating conditions, operational and accelerated Life tests and moisture resistance testing are part of the challenging evaluation. The ETP Final agreement test package can be found in resume in Fig.5.

TEST Nr	Evaluation Test Program Test Description	Precedence	Status
2Bi	Voltage Step Stress Test (VSST)	---	OK
2Bii	Temperature Step Stress Test (TSST)	2Bi	OK
2Biii	High Inrush Current Step Stress Test (SSST)	---	PASS
2Ci	Solderability / Adhesion	---	PASS
2Cii	Solderability /Humidity Sequence	---	PASS
2Cii	Moisture Resistance	---	PASS
3	Steady State Accelerate Life Test (T1/V1, T2/V2, T3/V3)	2Bi/ 2Bii	PASS
4	Operational Life Tests	---	PASS
5	Storage	---	PASS

Fig.5. Low Voltage ETP Final agreement and results

Components for each type were tested, subdivided in 5 main groups and the evaluation test program was completed according to the test plan. The components were submitted to several very harsh tests in temperature and humidity, including cycles testing with no major failures, and very good electrical stability: Thermal Shock and Mechanical Capability Tests as Solderability Adhesion, Solderability/ Humidity Sequence or Moisture Resistance. Capacitance shifts were observed as expected but were within limits and consistent with the known technology.
The Step Stress test group was designed to induce failures by voltage and temperature and the results were as expected for the in-situ polymer technology. It was possible to clearly identify the fault sites in the dielectric analysis performed on the failed parts, confirming the expected dielectric degradation with earlier breakdown failures for the highest voltage part type-16V.

Generally, the breakdown voltage of a capacitor increases linearly with the dielectric thickness. Manufacturers thus use, thicker dielectrics for higher voltage ratings. This general trend holds for solid electrolytic capacitors which employ MnO_2 as the solid cathode, where the dielectric thickness is proportional to the formation voltage. However, when the solid cathode system is intrinsically conductive polymer, the breakdown voltage versus formation voltage curve deviates significantly from this linear relationship as is evidenced by the graphs in Figure 6. This deviation from the ideal line suggests there is an interaction between the cathode and the dielectric resulting in a lower than expected breakdown voltage as the formation voltage increases.

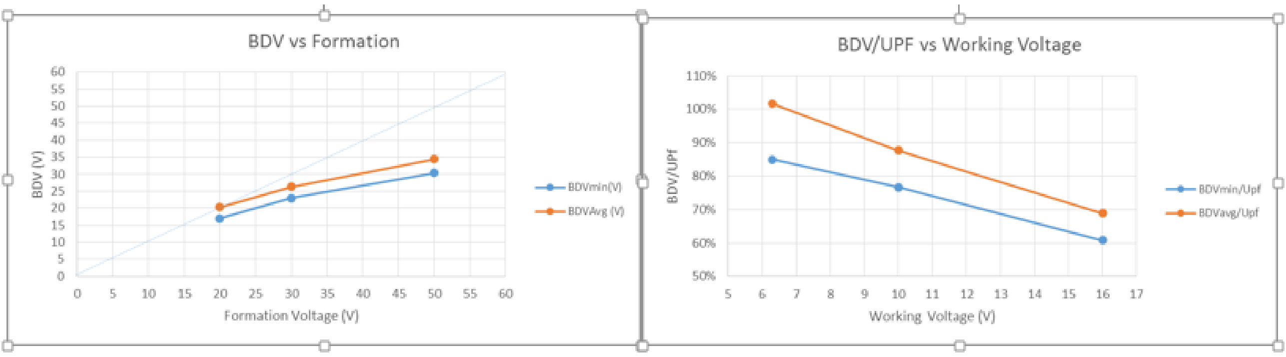


Fig.6. SSST BDV (V) vs Formation & SSST BDV/UPf vs Working Voltage for Existing Range Samples

The mechanism of failure in the in-situ polymerization is tentatively explained in literature using a metal-insulator-semiconductor model. Residuals from the in-situ chemical polymerization reaction between an oxidizer and monomer (Fig.7) can cause surface charge at the interface between the dielectric and the polymer affecting the potential barrier, and resulting in high DC leakage and low BDV. As an alternative to in-situ chemical polymerization, scientists discovered that if the conductive polymer was synthesized first and then applied to the tantalum pentoxide in the form of a pre-polymerized dispersion (Fig.8.), the voltage of the capacitor could be remarkably increased while retaining the low ESR and benign non burning failure mode.

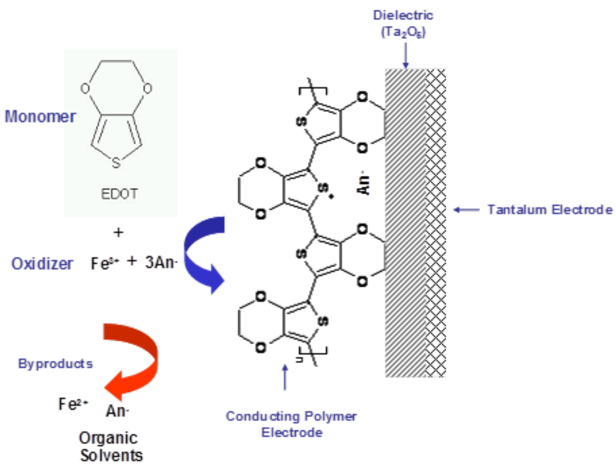


Fig. 7. Ta Capacitor with conductive Polymer electrode applied by *In-Situ* polymerization

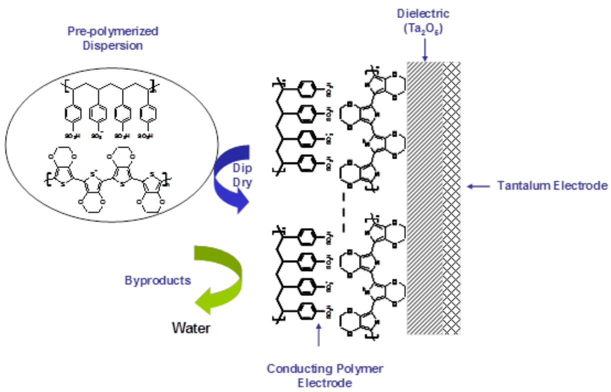


Fig.8. Ta Capacitor with conductive Polymer electrode applied from a pre-polymerized Dispersion

The improvement that can be achieved changing our current polymerization process, to one which utilizes a combination of the traditional in-situ polymer process and the pre-polymerized solution can be clearly shown by the Breakdown Voltage behavior is demonstrated in Fig. 9.

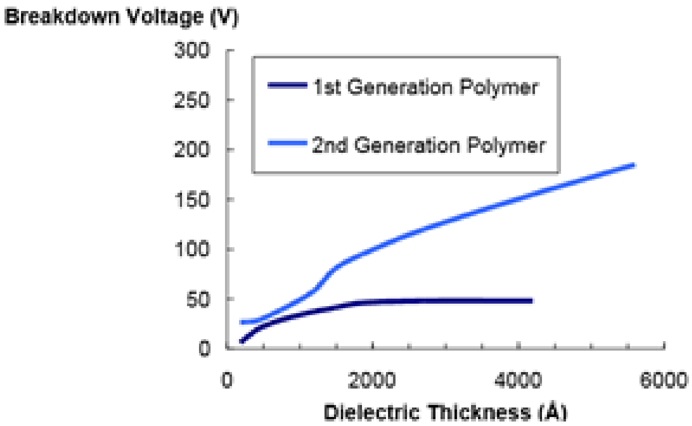


Fig. 9. Improvement in Breakdown Voltage (BDV) with 2nd-Generation Conductive Polymer (applied from pre-polymerized dispersion) vs. 1st-Generation Conductive Polymer (applied by in-situ oxidation of monomer to conductive polymer)

For 1st-generation materials, BDV's are less than 50 V no matter how thick the dielectric is made. For the 2nd-generation materials, BDV (and, therefore, working voltage) continues to increase with increasing dielectric thickness, making it possible to realize higher working-voltage Tantalum-polymer capacitors.
Group 3,4 and 5 – Endurance operation Life Testing groups, presented behavior – expected for the in-situ polymer technology as evidenced by way of example in Fig.10.

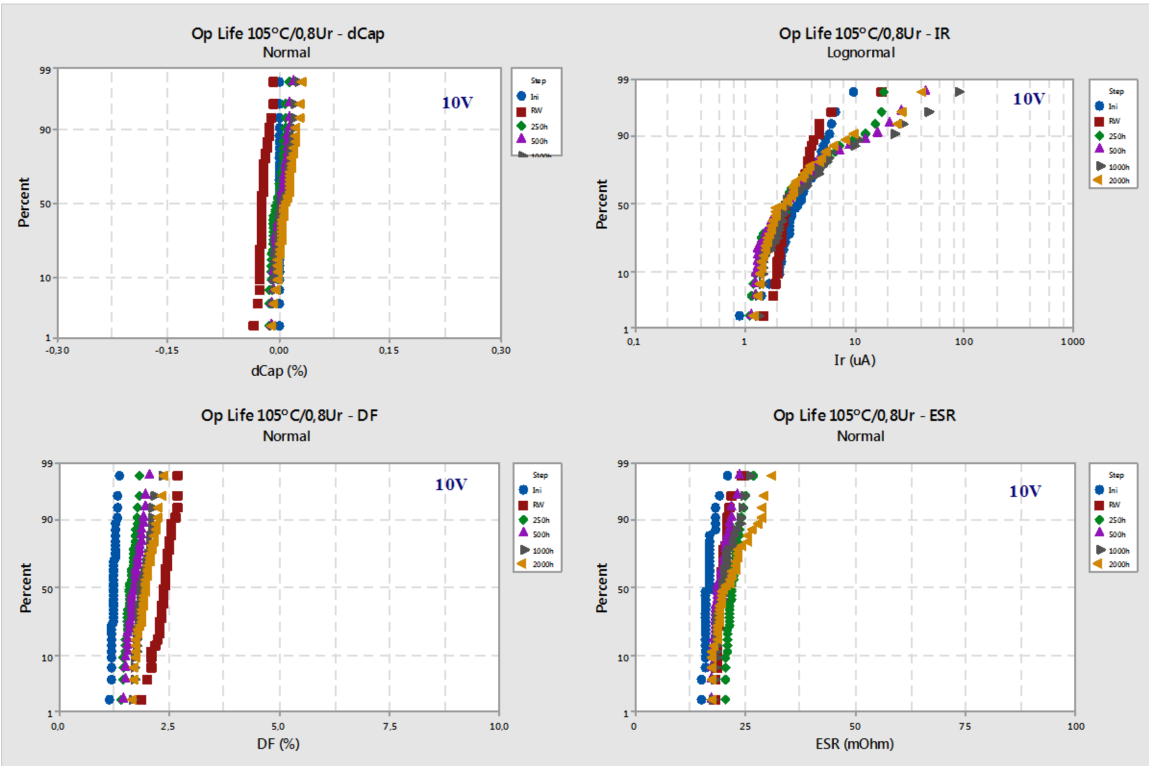
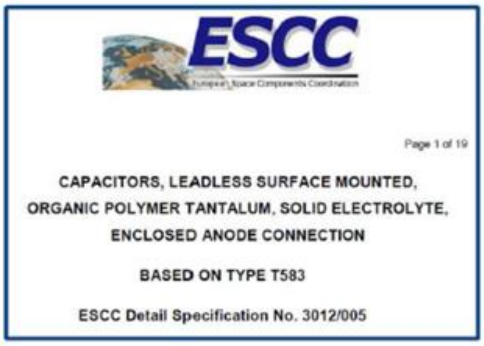


Fig.10 . Example of Op Life Results for 105ºC/0,Ur 2000hrs for a 10V Application Capacitor

From all the data retrieved form the ETP, a possible path was defined to overcome the identified weakness and degradation modes of the existing technology, and achieve the development, as intended, of very low ESR Polymer Ta Capacitor for High Voltage.

In parallel and in consideration of the good results achieved with the existing range samples, a small low voltage portfolio regulated by ESCC Details Specification nr. 3012/005 was proposed and approved for publication in European Preferred Part List (EPPL) – part2 issue 30. This same portfolio Fig.10. is undergoing further testing for QPL qualification.


ESCC

Page 1 of 19

CAPACITORS, LEADLESS SURFACE MOUNTED,
ORGANIC POLYMER TANTALUM, SOLID ELECTROLYTE,
ENCLOSED ANODE CONNECTION

BASED ON TYPE T583

ESCC Detail Specification No. 3012/005

Capacitance C_n (µF)	Rated Voltage U_R		
	6.3V	10V	16V
33			60, 70
47			70
68		45, 60, 100	
100	45	55, 80	
150	45, 55		

Fig. 10.ESCC nr 3012/005 and T583Low Voltage available portfolio

High voltage applications

The 2nd phase of the project sought to overcome the identified limitation to 16V of the existing Low Voltage range capability portfolio for the Évora plant, assuring a good breakdown Voltage (BDV) performance for application voltages up to 50V, and the reliability required for Space applications.

In order to overcome the identified weakness and degradation modes of the existing technology, a possible path to achieve the development, of very low ESR 25 to 50V polymer Ta Capacitors was defined and agreed with ESA.

Based on existing R&D developments within KEMET, a new hybrid process was studied with the combination of both in-situ polymerization and pre-polymerized solution deposition that through the reduction of the number of local chemical reactions, and consequent defect sites, improves the interface quality between the coating and dielectric, and therefore overcomes the BDV weakness and stabilizes its behavior.

In the production of the extended range sample, some of the points of possible improvements were immediately addressed in the new designs definition and on the process to be applied as an addition to the existing Process Identification Detail (PID) document. The most relevant to the success of this project where the modified cathode layers polymerization process and the optimized aging process across lower temperature and higher aging ramp and hold times.

New samples of extended rated voltage were manufactured (25 to 50V) with this 2nd generation polymerization process and were proposed for evaluation with the target to establish a Qualification roadmap for the 50V extended rated voltage industrialization- Fig.11.

	Rated Voltage					
Cap	16	20	25	35	50	63
6,8						
10					D (125mΩ)	
15			D	D (100mΩ)		
22		D	D			
33		D	D (100mΩ)			
47		D				
68						

Legend:
Corners — Parts submitted for ETP testing
Sister part types

Fig.11. Portfolio for Extended Voltage Range Qualification

A complete electrical characterization was started for the 3 part types studied to understand the effectiveness of the improvements, and again the Breakdown voltage performance was evaluated across the working voltage. As we can observe from the graphs in Fig.12., the median BDV is still around 3 times rated voltage and the minimum BDV is around 2 times rated voltage, which is in line with the low voltage polymer behavior characterized for the existing range.

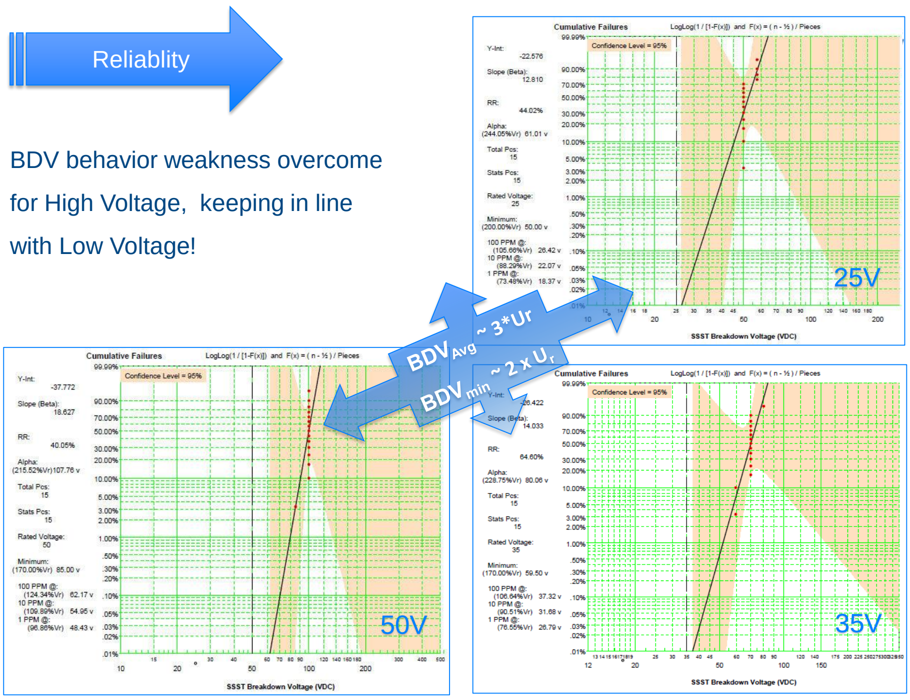


Fig.12. High Inrush Stress Step Test for Extended High Voltage Range

With the new process it has been shown that we are able to overcome the limitation of a decreasing BDV versus working voltage ratio that would led us to lower working voltages, and therefore propose and validate these extended working voltages-Fig.13.

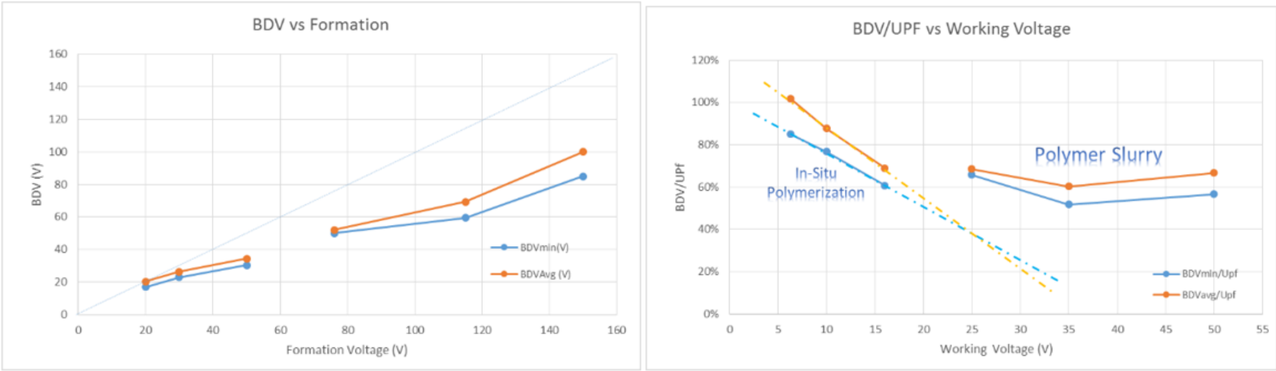


Fig.13. SSST BDV (V) vs Formation & SSST BDV/UPf vs Working Voltage for for Existing Range and Extended Range

The new extended range Part numbers started the Evaluation Test Program, according Fig.14, and the results will determine if additional improvements or optimization are required. Nevertheless the good results achieved allow us to propose a small portfolio (Fig.10, above) to proceed for qualification.

TEST Nr	Evaluation Test Program Test Description	Precedence	Status
2A	Thermal Shock	---	PASS
2Bi	Voltage Step Stress Test (VSST)	---	OK
2Bii	Temperature Step Stress Test (TSST)	2Bi	On-Going
2Biii	High Inrush Current Step Stress Test (SSST)	---	PASS
2Cii	Moisture Resistance	---	PASS
3	Steady State Accelerate Life Test (T1/V1, T2/V2, T3/V3)	2Bi/ 2Bii	Not Started
4	Operational Life Tests	---	Not Started
5	Storage	---	Not Started

Fig.14. High Voltage ETP Final agreement and status

TA SMD CAPACITORS WITH MNO_2 COUNTER ELECTRODE

The need for higher temperature compliance in electronics applications has grown widely over the years and reached new fields of application. Day after day electronics makes its way in all applications, supporting and replacing existing systems, making industrial areas as Avionics, Space, Defense and Automotive join down-hole oil and gas industry in the quest for high reliability electronic components under harsh environment conditions.

Solid Ta capacitors with manganese dioxide as counter electrode have proven their capability and Stability for high temperature applications reaching 150ºC, 175ºC, 200ºC & 230ºC, and KEMET offers the latest in high temperature capacitor technology providing solutions for extreme temperature applications with families T498/ T499/ T500 & T502 (1^{st} to market 230ºC Ta SMD MnO_2 technology none hermetic!).

The extended capability to 150ºC maximum operational temperature with Ta SMD MnO2 components with ESA qualification allow space application designers to use the high volumetric efficiency from these components with extended life capability and/or safety margin. This new extension – T483, is complementary to the well-established and known technology in the field.

Nine corner types were selected from existing MnO_2 portfolio offering (4 to 50V), with representatives of all case sizes, and proposed for evaluation for 150ºC, with agreed ETP that is undergoing – Fig. 15. For the purpose of this discussion are presented some examples of available reliability data and behavior of the tested range under temperature.

TEST Nr	Evaluation Test Program Test Description	Precedence	Status
2A	Thermal Shock	---	PASS
2Bi	Voltage Step Stress Test @ 150ºC (VSST)	---	OK
2Bii	Temperature Step Stress Test @ Ur (TSST)	2Bi	OK
2Biii	High Inrush Current Step Stress Test (SSST)	---	PASS
2Ci	Solderabilty/ Adhesion	---	Not Started
2Cii	Solderabilty/ Humidy Sequence	---	PASS
3	Steady State Accelerate Life Test (T1/V1, T2/V2, T3/V3)	2Bi/ 2Bii	Not Started
4	Operational Life Tests (@ 85ºC/ 150ºC)	---	Not Started
5	Storage @ 150ºC	---	Not Started

Fig.15. 150ºC MnO_2 ETP Final agreement and status

Fig. 16. Shows the characterization in temperature of ESR and DC Leakage for the selected range with a performance very consistent with expectation for MnO2 technology, proving that the advancements in materials, design and testing do allow us to target for optimal performance in applications with operating temperatures up to 150ºC.

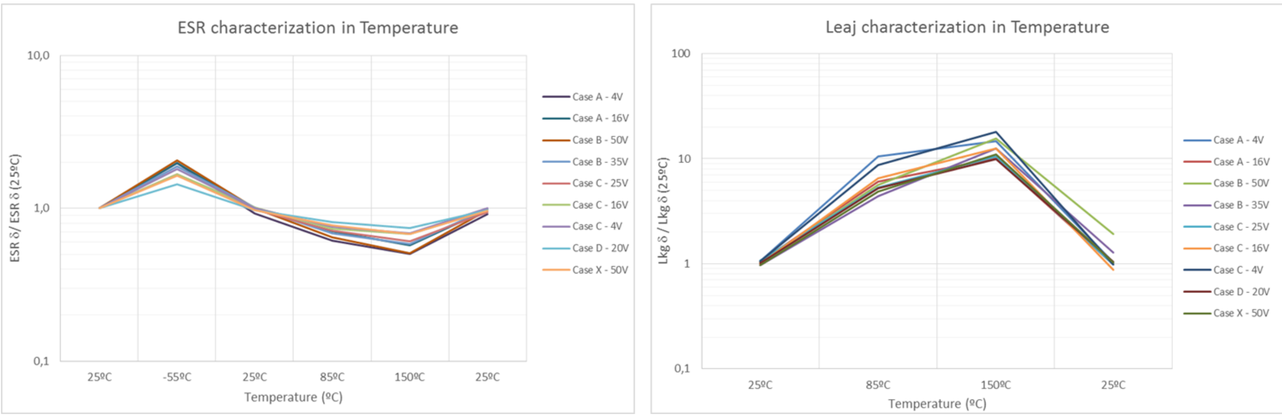


Fig.16. Temperature Stability data for 150ºC

Temperature Step Stress Test as part of group 2B of ETP intend to determine and push to the limit the dielectric capacity. At Rated voltage temperature step increase of 168H were performed with very good results up to 200ºC – Fig. 17.

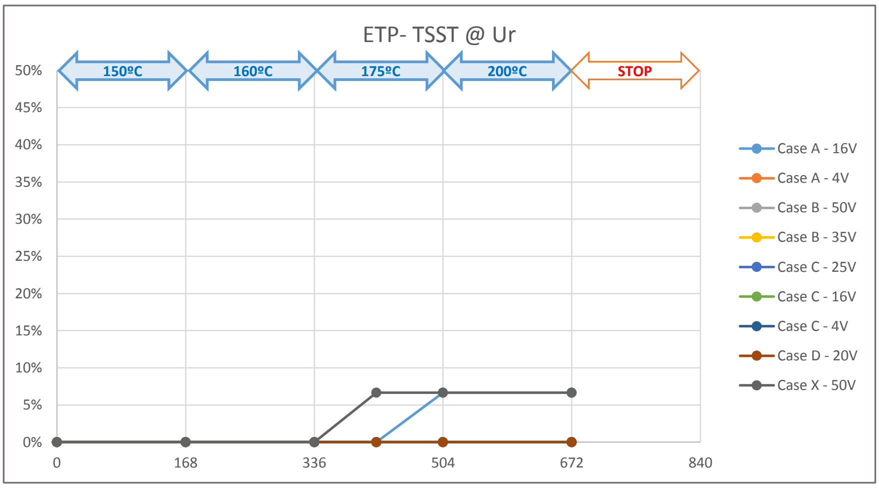


Fig.17. ETP - Temperature Step Stress Test for MnO_2/150ºC

The next step will be to determine and agree with ESA accelerated life test – Group 3, conditions in Temperature and Voltage to further characterize this proposed range for high temperature applications.

KEMET will continue its development efforts qualifying components of SMD Tantalum technology for Space applications with increasing harsh environmental conditions

ACKNOWLEDGMENTS

This work, with emphasis to Ta SMD capacitors with polymer counter electrode for High Voltage application was possible through a development project sponsored and supported by ESA and Portugal delegation Space Incentive Program.

REFERENCES

[1] A.Tomás, R.Monteiro, J.Vacas, C.M.Caetano, D. Lacombe, O. Perat, "New SMD Ta Capacitors with Polymer Counter Electrode for Space Applications", CSME, 2014.
[2] KEMET Electronics Corporation, Greenville, US, "High Voltage solid electrolytic capacitors using conductive polymer slurries", Y.Qiu, R.Hahn, K.Breeneman, Int.CI. H01G9/00, US 7.563.290. B2, 21 July 2009.
[3] J. Young, J. Qiu, R. Hahn, "High Voltage Tantalum Capacitors", CARTS 200.
[4] J. Young, "Last decade's MnO_2 experiences are not this decade's polymer reality", 2016 AEC Reliability Workshop
[5] KIT KEMET Institute of Technology 2015
[6] www.kemet.com
[7] ESCC3012/005, https://escies.org/specfamily/view
[8] Work Package reports – ESTEC Contract nº 4000105501/12/NL/SFe, "polymer Tantalum Capacitor (very low ESR)"